Catalytic wet air oxidation of a high strength *p*-nitrophenol wastewater over Ru and Pt catalysts: Influence of the reaction conditions on biodegradability enhancement

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ABSTRACT

p-Nitrophenol (PNP) is widely used as a raw material in several industries, therefore it can be released to the environment, being mandatory the treatment of the PNP-contaminated industrial wastewaters. In this sense, the influence of temperature, oxygen partial pressure, type of catalyst, pH and ionic strength on the wet air oxidation (WAO) of a highly concentrated PNP wastewater was studied. Several 480 min batch tests have been performed and four Pt and Ru-based catalysts have been tested. The PNP elimination, total organic carbon (TOC) abatement and the intermediates distribution were monitored. Moreover, respirometric screening tests were completed after each experiment to assess the biodegradability enhancement of the catalytic WAO (CWAO) treated effluents. The results showed that PNP elimination was higher than 90% in most cases, being the temperature the most important operating parameter upon CWAO. Additionally, all the catalysts showed a similar behaviour in terms of PNP and TOC conversions. Besides, CWAO increased the biodegradability by more than 50% in most of the tested conditions, being the carboxylic acid fraction the key factor to be taken into account, as the best biodegradability enhancement was observed when this fraction was the highest. The partial pressure of oxygen had a negligible effect on the biodegradability enhancement. The ionic strength influence over the CWAO was studied and even though it did not affect the CWAO performances, the presence of NaCl in the solution resulted in a decrease of the effluent biodegradability. In terms of pH, the most suitable scenario was the one with no pH adjustment. Conclusively, this work demonstrated that an integrated CWAO and biological treatment would allow an easy removal of PNP and the intermediates formed during the first step of the treatment, being the best CWAO conditions for this pre-treatment to work at 180 °C under stoichiometric oxygen pressure (i.e. 7.6 bar of oxygen partial pressure) with a Ru/TiO$_2$ catalyst.

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1. Introduction

Nowadays, industrial wastewaters represent a big challenge for researchers and technology developers. Intensive research is being made over removal of phenol and substituted phenols from wastewaters, not only because of their toxicity to the environment, but also, because of the large volumes disposed worldwide. For example in Europe more than 2000 ton y^{-1} of phenolic compounds are released as indirect emissions to the environment [1]. In this work, *p*-nitrophenol (PNP) has been selected as a model compound, because it is one of the phenolic compounds included in the list of High Volume Production Chemicals made by the Organization for Economic Cooperation and Development [2]. PNP is primarily used in the N-acetyl-*p*-aminophenol production, which is a raw material in paracetamol production, as a chemical intermediate for the manufacture of insecticides (e.g. methyl and ethyl parathion), azo and sulfur dyes or leather preservatives [3,4]. Besides its wide uses, PNP is highly toxic for the environment and human beings since repeated exposure may cause injury to blood cells, damage to the nervous central system and have mutagenic effects; whereas long-term exposure could cause large damages to kidney and liver [5].

Biological treatment has been proved to degrade effectively PNP by using sequencing batch reactors (SBR) treating up to 400 mg PNP L^{-1}; however, the aerobic PNP degradation can be limited by substrate inhibition when high-strength concentrations of PNP wastewaters are treated [6–8].

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In this sense, and among many others processes, catalytic wet air oxidation (CWAO) is an efficient technology which has been used to treat wastewaters containing organic compounds which are highly toxic or too concentrated to be treated only with biological treatment and it is used as one of the most economical and environmental-friendly oxidation process [9]. The process consists in oxidising the pollutants under oxygen pressure at elevated temperature and in the presence of a catalyst, which can be metal oxides or noble metals, either heterogeneous or homogeneous [10]. The process can be directed in two different ways obtaining: (i) a complete mineralization of the organic pollutants into CO_2, N_2, H_2O and mineral salts or (ii) an increase of the effluent biodegradability by directing the conversion of the toxic organic compounds towards the formation of more biodegradable products, such as carboxylic acids [11]. CWAO of substituted phenols has been widely studied using supported noble metals (Pd, Pt, Ru over ZrO_2, TiO_2, CeO_2, activated carbon and γ-Al_2O_3), CeO_2-supported Cu and Fe or bare activated carbons as catalysts, with temperature and pressure conditions ranging from 120 to 180 °C and 0.5 to 1.6 MPa of O_2 and focusing primarily on the performances of the catalyst, the pollutant conversion, the distribution of the partial oxidation products and more recently, on the biodegradability enhancement [9].

Also, combinations of other oxidation processes, mainly Fenton and photo-Fenton, with biological treatment have been successfully studied for several industrial wastewaters [11]. Moreover, ozonation of PNP has proven to enhance the biodegradability of the effluent [12]. In addition, some of our previous works have demonstrated the feasibility of using WAO and CWAO to increase the biodegradability of phenolic effluents [13,14].

In particular, for PNP oxidation, commercial activated carbons have been used as direct catalytic materials for PNP degradation in a trickle bed reactor, obtaining practically no conversion at 140 °C under 2 bar of O_2 partial pressure [15]. Other studies, using AC as catalyst as well, obtained nearly 80% of PNP conversion, but at the cost of increasing temperature and pressure [16]. The same is observed when metal catalysts supported on metal oxides are used [17]. The reaction intermediates were shown to be mainly hydroquinone, catechol, *p*-benzoquinone and carboxylic acids.

However, prior to discharge of the CWAO effluents into a conventional wastewater treatment plant (WWTP), the biodegradability and the toxic and inhibitory effects of these effluents have to be assessed to prevent any malfunctioning of the WWTP and to protect the biomass. To this end, several techniques and instruments can be used. BOD_5/COD ratio provides an approximate index of the proportion of the organic substances in the wastewater that are biodegradable under aerobic conditions; it is one of the most used techniques to determine the increase of biodegradability of the effluents [18]. Microtox® is also used successfully to determine the toxicity of an effluent, but it can result in an overestimation of the

EC_{50} values [19]. The Zahn–Wellens test has also been used for toxicity screens, but it is time consuming and can underestimate this effect [20]. Finally, respirometry uses the biomass directly taken from a WWTP, therefore, the effects of a determined influent to the WWTP could be evaluated directly on the receiving sludge [21]. Moreover, with respirometric tests, the influent organic matter can be classified as readily biodegradable, inert or toxic/inhibitory according to its effect on the receiving sludge [14].

Accordingly, the main objective of this work was to treat a high-strength PNP wastewater using CWAO and supported Ru and Pt catalysts, which have been used effectively for other substituted phenols [22]. CWAO was performed as a pre-treatment to increase the biodegradability of the influent before a subsequent biological treatment. To fix the most suitable conditions for a combined chemical and biological treatment of PNP contaminated wastewaters, the influence of temperature, O_2 partial pressure (P_{O_2}), pH, saline content and catalyst formulation on the PNP oxidation was assessed. Also, the biodegradability of these effluents was established through respirometric tests, providing valuable information to determine the most favourable conditions to perform a combined chemical and biological treatment on this type of wastewater. As far as the mineralization of PNP was not the pursued objective, but the optimization of the biodegradable fraction, the distribution of the reaction intermediates, which is directly related to the biodegradability enhancement, was also studied.

2. Materials and methods

2.1. Experimental set up for WAO and CWAO experiments

Experiments were performed in a 280 mL batch reactor made of Hastelloy. The reactor was equipped with a magnetically driven stirrer working at a constant velocity (1000 rpm), high enough to avoid external diffusion problems. Temperature was maintained constant in the range of 120–180 °C using an electric jacket. For all the experiments, 140 mL of PNP solution at a given concentration and a certain amount of catalyst were introduced in the reactor. The solution was repeatedly purged with argon to remove any trace of oxygen and heated up to the desired reaction temperature under stirring. Once the temperature reached a steady state value, the stirrer was stopped and synthetic air (20 vol. % O_2 and 80 vol. % N_2) was introduced in the reactor up to the desired pressure. The stirrer was switched back on and this time was considered as the time zero for the reaction.

Different operation conditions were evaluated with the objective to compare their influence on the intermediates distribution and the biodegradability enhancement (Table 1). All experiments were performed with an initial PNP concentration of 5 g L^{-1}, corresponding to an initial pH of 4.6 (without any pH adjustment,

Table 1
Experimental conditions tested.

AOP	Temperature (°C)	Catalyst	P_{O_2} (bar)	O_2/PNP stoichiometric molar ratio	Initial pH	[NaCl] (g L^{-1})
WAO	120	–	7.6	1.0	4.6	0
	160	–	7.6	1.0	4.6	0
	180	–	7.6	1.0	4.6	0
CWAO	120	Ru/TiO_2	7.6	1.0	4.6	0
	160	Ru/TiO_2	7.6	1.0	4.6	0
	160	Ru/TiO_2	11.4	1.5	4.6	0
	180	Ru/TiO_2	7.6	1.0	4.6	0
	180	Ru/TiO_2	11.4	1.5	4.6	0
	180	Ru/TiO_2	7.6	1.0	2.0	0
	180	Ru/TiO_2	7.6	1.0	8.0	0
	180	Ru/ZrO_2	7.6	1.0	4.6	0
	180	Pt/TiO_2	7.6	1.0	4.6	0
	180	Pt/ZrO_2	7.6	1.0	4.6	0
	180	Ru/TiO_2	7.6	1.0	4.6	25

Table 2
Specifications of the commercial supports used in this work.

Support	TiO$_2$ DT51	ZrO$_2$ Mel
Supplier	Millennium	Melcat chemical
Crystalline phase	Anatase	Monoclinic
Granulometry	Powder: 0.2–5 μm	Powder
S_{BET} (m^2 g^{-1})	80–100	90
Average pore diameter (nm)	9	8–9
Incipient volume (mL g^{-1})	1.1	0.5
pH$_{pzc}$	4.4	6.1

except wherever indicated in the text) and a stoichiometric oxygen partial pressure to achieve complete mineralization (except where indicated). All CWAO experiments were carried out using 0.5 g of a 3 wt.% metal catalyst (particle size: 20–40 μm), corresponding to a catalyst concentration of 3.6 g$_{catalyst}$ L^{-1}. The total pressure was also kept constant all along the experiment and hence re-adjusted whenever necessary, especially after each liquid sample withdrawal. The effect of temperature on the PNP treatment, both in the absence and in the presence of a catalyst, was tested at 120, 160 and 180 °C. The effect of the catalyst formulation was also tested using four different heterogeneous catalysts: Ru/TiO$_2$, Ru/ZrO$_2$, Pt/TiO$_2$ and Pt/ZrO$_2$. Other sets of experiments were performed to study the effect of the O$_2$ partial pressure (P_{O_2}) at 160 °C and 180 °C. The initial pH effect was studied at three different values: 2.0, 4.6 and 8.0, adjusting the pH with H$_2$SO$_4$ or NaOH when needed. Finally, the impact of the solution ionic strength was studied by addition of a 25 g L^{-1} NaCl solution to the reaction mixture.

Liquid samples were periodically withdrawn from the reactor and further analysed to follow the evolution of the PNP concentration and the formation of the reaction intermediates. Moreover, once the reaction was stopped, the reactor was opened after reaching ambient conditions and its content was collected for further biodegradation analysis.

2.2. Catalyst preparation

Heterogeneous catalysts, based on ruthenium and platinum, were used in this study. Each metal was supported on two different metal oxides, namely TiO$_2$ and ZrO$_2$. Both supports are commercially available and their specifications are summarised in Table 2.

Ruthenium based catalysts were prepared via incipient wetness impregnation [23]. The support was impregnated with a Ru(NO)(NO$_3$)$_3$ solution, using a volume corresponding to the incipient volume only. The metal loading was fixed at 3 wt.%. The solution was added to the support drop by drop under constant and vigourous stirring to guarantee an homogeneous dispersion of the metallic phase on the support.

Platinum based catalysts were prepared through the liquid impregnation method [24], using Pt(NO$_3$)$_2$ as the metal precursor. The Pt content was also fixed at 3 wt.%. The mixture was stirred for 1 h at room temperature and then introduced in a rotary evaporator for 2 h at 60 °C under reduced pressure (ca. 150 mbar).

The residual water was finaly eliminated by drying overnight in an oven set at 120 °C. Both catalysts were reduced under flowing H$_2$ (15 L h^{-1}) at 300 °C for 2 h. Finally, they were stored under argon [25].

2.3. Analytical methods and materials

Several analyses were performed in order to determine the total organic carbon (TOC) abatement, the PNP conversion and the reaction intermediates formation in each experiment.

PNP and all the others compounds used in this work were of analytical grade (Sigma–Aldrich, France). PNP and the reported intermediates in the PNP CWAO such as: 4-nitrocatechol (4-NC),

phenol, 2,4-dinitrophenol (2,4-DNP), biphenyl, p-benzoquinone (p-BQ), hydroquinone, catechol, succinic acid, maleic acid, fumaric acid, acetic acid, acrylic acid, formic acid, malic acid and glycolic acid were monitored [14,16,26]. For the CWAO effluents, analyses were performed using high performance liquid chromatograph (HPLC) with a Shimadzu Prominence HPLC line equipped with an UV/vis detector (UV SPD-20A). Compounds concentration was calculated by means of calibration curves established with external standards. For PNP and quinone-like compounds the column was a C18 QS Uptisphere 3 HDO (INTERCHROM, 100 × 2 mm, 3 μm). The flow rate was set at 0.3 mL min^{-1} and the UV/vis detector at 254 nm. The mobile phase was a mixture of methanol and distilled water (2.5:97.5 v/v) acidified with H$_3$PO$_4$ (0.002 N). For carboxylic acids, the column was an ICSepCoregel 107H Transgenomic (7.8 × 300 mm). In this case, the flow rate was set at 1.0 mL min^{-1} and UV/vis detector was set at 210 nm. The mobile phase was distilled water acidified with H$_2$SO$_4$ (0.005 N). In both cases, the injection volume was 20 μL and the column was maintained in an oven at 40 °C. Samples were centrifuged at 60,000 rpm for 30 min prior to analysis. The standard deviation is 0.5%.

TOC and total nitrogen (TN) were measured using a Shimadzu TOC V$_{CSH}$ analyser, which was also provided with a TN analyser module (TNM-1). The oven was set at 720 °C and the amount of CO$_2$ produced was measured by an infrared detector. The TN module was set at 50 °C and used a chemiluminescent detector to measure nitrogen species. The TOC and TN values were calculated by means of calibration curves established with external standards. Two replicates of each sample were systematically measured and the average value was reported. The standard deviation was 4% in both cases.

Ionic chromatography analysis was used to measure nitrite and nitrate in the samples. The equipment used was an 881 ICpro Metrohm Compact, equipped with an auto sampler and a module for the analysis of the anions and the detection was performed by conductivity. The mobile phase was a solution of 3.2 mM of Na$_2$CO$_3$ and 1.0 mM of NaHCO$_3$. The column used was a METROSEP A Supp 5 150/4.0, the flow rate was set at 0.7 mL min^{-1}, column temperature was set at 25 °C and the injection volume was 20 μL.

pH analysis on the solution withdrawn from the reactor as a function of time were also performed with a PHM240 pH/ion Meter from Radiometer Analytical. The metal content on the catalyst was determined by ICP-OES.

2.4. Experimental set up for respirometric experiments and determination of biodegradation parameters

Respirometric tests allowed the determination of the readily biodegradable fraction of the chemical oxygen demand (COD) of the final effluents collected at the end of each WAO and CWAO experiments. The experiments were performed in a LFS-type of respirometer, being the equipment and principle described elsewhere [13]. Temperature and pH were set at 26 ± 0.5 °C and 7.5 ± 0.1, respectively.

The method for the determination of the biodegradation parameters was adapted from another study [13]. For each respirometric test, biomass was taken from a full scale municipal WWTP located in the Barcelona area (Spain). Then, the sludge was aerated during 2 h before experiment to remove any trace of soluble COD in the liquid. Three respirometric tests were performed to assess the biodegradability and the toxic or inhibitory effects of the selected effluents. The process might be summarised as follows: Run 1: 47 mg COD L^{-1} of sodium acetate, used as control substrate was added; Run 2: once the pulse in Run 1 was consumed, a pulse of the WAO or CWAO effluent was added; Run 3: the pulse on run 1 was repeated after pulse in run 2 was completely depleted or after 1 h of contact time. The toxicity and inhibition effects can be assessed
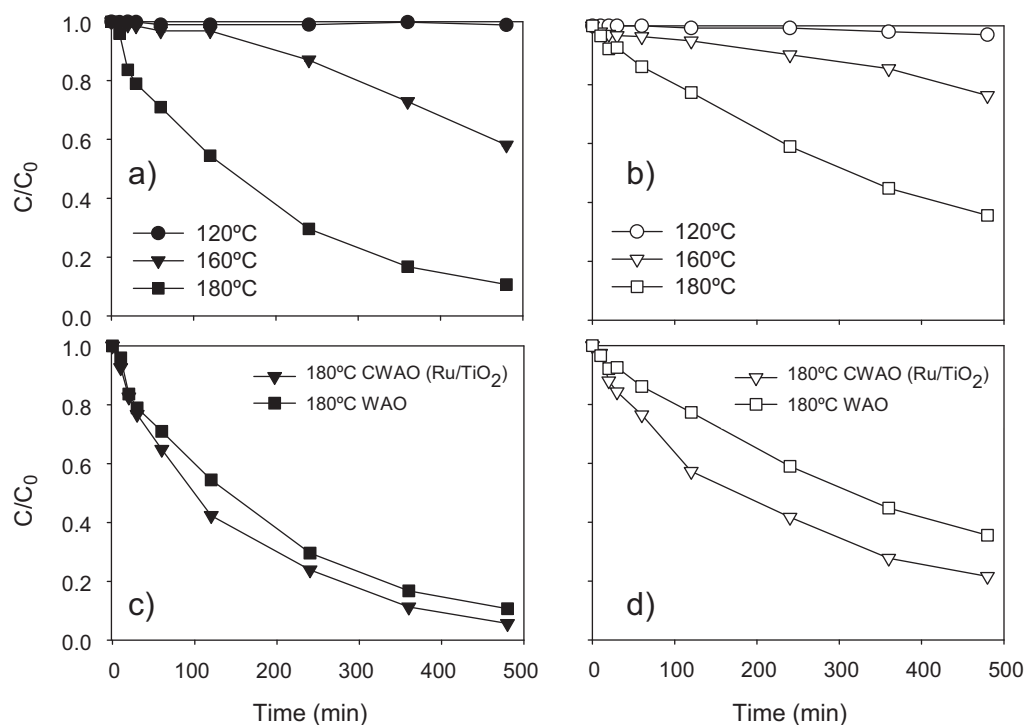
Fig. 1. Evolution of the relative PNP and TOC concentrations as a function of time upon WAO and CWAO experiments under different reaction conditions. (a) PNP (full symbols) and (b) TOC (empty symbols) upon WAO at 120 °C – 7.6 bar of oxygen partial pressure (circles), 160 °C – 7.6 bar of oxygen partial pressure (triangles) and 180 °C – 7.6 bar of oxygen partial pressure (squares). (c) PNP (full symbols) and (d) TOC (empty symbols) upon WAO (squares) and CWAO (triangles) at 180 °C – 7.6 bar of oxygen partial pressure. Initial PNP concentration = 5 mg L^{-1}, 0.5 g of Ru/TiO$_2$. No pH adjustment. No NaCl.

by comparing the specific oxygen uptake rate (SOUR) profiles and the oxygen consumed (OC) in runs 1 and 3 as follows:

$$\%\text{Toxicity} = \left(\frac{(OC_{RUN_1}) - (OC_{RUN_3})}{(OC_{RUN_1})} \right) \times 100 \qquad (1)$$

$$\%\text{Inhibition} = \left(\frac{(SOURmax_{Run_1}) - (SOURmax_{Run_3})}{(SOURmax_{Run_1})} \right) \times 100 \qquad (2)$$

The biodegradability was measured as the percentage of readily biodegradable COD (COD$_{RB}$) according to the procedure described by Suárez-Ojeda et al. [14]. COD$_{RB}$ can be calculated from Eqs. (3) and (4), using the heterotrophic yield coefficient ($Y_H = 0.71 \pm 0.2$) obtained in a previous work [14] for a similar activated sludge and the oxygen consumed (OC) measured during each respirometry:

$$COD_{RB} = \frac{OC}{1 - Y_H} \qquad (3)$$

$$\%COD_{RB} = \frac{COD_{RB}}{COD_{ADDED}} \times 100 \qquad (4)$$

COD$_{ADDED}$ corresponds to 47 mg COD L^{-1} for all the effluents tested.

Moreover, the biodegradability enhancement was considered as the difference between the %COD$_{RB}$ in the influent and in the effluent after WAO or CWAO:

Biodegradability enhancement

$$= (\%COD_{RB})_{effluent} - (\%COD_{RB})_{influent} \qquad (5)$$

It should be mentioned that the %COD$_{RB}$ of a PNP sample of 47 mg COD L^{-1} was completely null. Consequently, the biodegradability enhancement after each experiment was directly the %COD$_{RB}$ measured on the CWAO effluent.

## 3. Results and discussion

3.1. PNP degradation by WAO and CWAO

3.1.1. Effect of temperature on WAO and CWAO

The first step was to determine the thermal stability of the PNP molecule. This was evaluated at 180 °C in the absence of any catalyst and using 50 bar of argon instead of air. After 24 h, no PNP degradation was observed (data not shown). Consequently, any PNP degradation observed in the presence of air should result from oxidation and not from the thermal cracking of the PNP molecule.

To study the influence of temperature, WAO experiments, in the absence of any catalyst, were carried out at 120, 160 and 180 °C using the oxygen partial pressure corresponding to the stoichiometric amount required for complete mineralization. PNP and TOC conversions were significantly affected by temperature (Fig. 1a and b). For instance, the PNP conversion after 480 min reaction markedly increased with temperature, from a negligible value at 120 °C to 41 ± 1 and $90 \pm 1\%$ at 160 and 180 °C, respectively. The difference between the PNP and TOC conversions indicated the presence of partially oxidised compounds such as 4-NC, phenol, p-BQ, catechol and several carboxylic acids (succinic, fumaric and acetic acids). The increase in temperature also affected the reaction intermediates distribution, increasing the carboxylic acids fraction as temperature increased (the reader is kindly referred to Fig. S1 in supporting information to see an example of the available data). For the N-species, NO$_2^-$ from PNP, 4-NC and 2,4-DNP molecules is oxidised to NO$_3^-$, which was the only N-compound detected. TN remained constant in all the experiments.

The effect of the use of a catalyst to improve the reaction rate and the final PNP conversion was assessed by comparing the WAO experiment performed at 180 °C with the CWAO experiment carried out under the same operational conditions but using Ru/TiO$_2$ as catalyst (Fig. 1c and d). The use of the Ru/TiO$_2$ catalyst resulted in
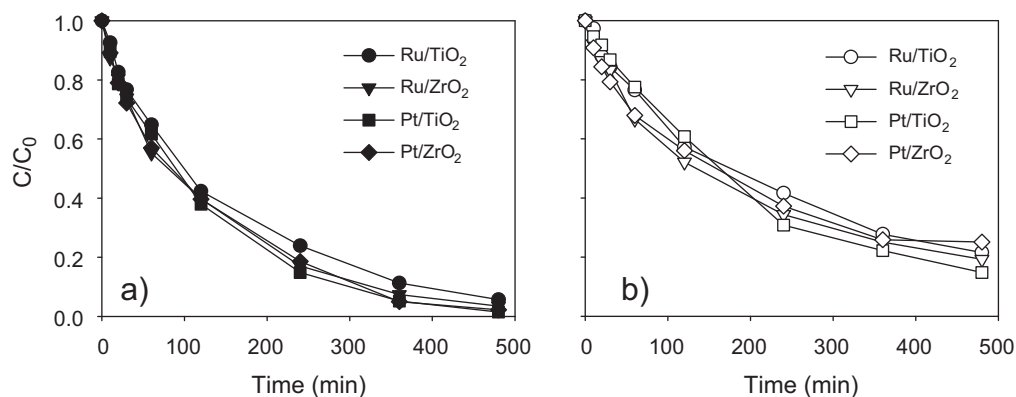
Fig. 2. Evolution of the relative PNP and TOC concentrations as a function of time upon CWAO experiments using different catalyst. (a) PNP (full symbols) and (b) TOC (empty symbols) over Ru/TiO$_2$ (circles), over Ru/ZrO$_2$ (triangles), over Pt/TiO$_2$ (squares) and over Pt/ZrO2 (diamonds) at 180 °C – 7.6 bar of oxygen partial pressure. 0.5 g of catalyst. No pH adjustment. No NaCl.

a low increase of the PNP conversion, but a higher TOC conversion (20 ± 4%), showing that the use of a catalyst acted on the intermediates distribution. The reaction is pushed further towards the formation of carboxylic acids at the end of the experiment (data not shown).

In this case, the activation energy was directly derived from the Arrhenius plot (logarithm of the reaction rate versus the inverse temperature) and calculated to be ca. 57 ± 1 kJ mol^{-1} which is about half of the one calculated for the WAO experiments (101 ± 2 kJ mol^{-1}). Both values are comparable to the values reported in the literature for PNP oxidation [27]. Compared to the activation energy of the CWAO of 2-chlorophenol over Ru/ZrO$_2$ (36 kJ mol^{-1}) [28] and the CWAO of phenol over Pt–Ru/C (34 kJ mol^{-1}) [27], PNP seems to be much more refractory to oxidation. These findings are in agreement with what has been reported by Pintar and Levec [29], where the PNP degradation rate was shown to be slower than for phenol and 2-chlorophenol under the same oxidation conditions. Moreover, PNP contains a nitro group, which is an electron withdrawing substituent that strongly deactivates the benzene ring. This fact explains the high resistance to oxidation of PNP [15]. Moreover, it is well known that some carboxylic acids are refractory to CWAO. For example, the activation energy for the CWAO of succinic acid is 124 kJ mol^{-1} [25]. Consequently, it is expected that the reaction will not proceed further until complete mineralization under such reaction conditions. Nevertheless, the typical carboxylic acids present in the CWAO effluents from phenolic compounds (i.e. formic, succinic and acetic acid) were found to be readily biodegradable compounds, being suitable for a further biological treatment [13].

3.1.2. Effect of the catalyst formulation

As far as the use of a Ru/TiO$_2$ catalyst enhanced the fraction of carboxylic acids in the effluent, we decided to test the activity of different Ru and Pt catalysts supported over TiO$_2$ and ZrO$_2$ to assess the possible effect of the type of catalyst on the PNP oxidation. The metal loading was fixed at ca. 3 wt.% for all catalysts and the operational conditions were: 180 °C, 7.6 bar P_{O_2} and an initial PNP concentration of 5 g L^{-1}. To evidence any catalyst leaching, Ru, Pt, Zr and Ti concentrations were measured in the effluents: Ti and Zr concentrations were systematically below the ICP-OES detection limit (<0.1 mg L^{-1}), whereas the average leaching of Ru and Pt was 2.4 ± 0.2 and 1.5 ± 0.2% of the initial metal content, respectively. Ruthenium and platinum catalysts supported on Ce, Ti or Zr oxides are reported to be stable in the CWAO of organic compounds with low concentration of metal in the effluents or concentrations even below the detection limit [24,30]. Nevertheless, it is also reported in the literature that some nitrogen species, with a single pair of

electrons on the nitrogen atom, can create a strong chemical bond with the metal atoms [23]. However, none of these species were detected in the effluents for the tested catalysts.
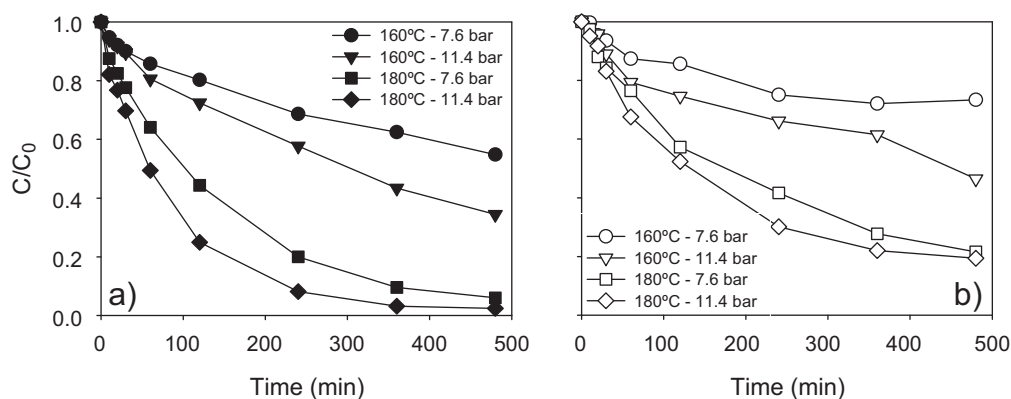
The initial reaction rate was of the same order of magnitude for Ru/TiO$_2$, Ru/ZrO$_2$, Pt/TiO$_2$ and Pt/ZrO$_2$, i.e. 18, 20, 22 and 22 mol$_{PNP}$ mol metal^{-1} h^{-1}, respectively; whereas the final PNP conversion after 480 min reaction was of 94 ± 1, 97 ± 1, 98 ± 1 and 98 ± 1%, respectively (Fig. 2a). Looking at the TOC conversion after 480 min reaction, the values obtained were 78 ± 4, 81 ± 4, 81 ± 4 and 80 ± 4%, respectively (Fig. 2b). These results showed that there is no significant difference between the PNP and TOC conversions, nor in the intermediates distribution, despite of the use of different catalysts. However, in other studies, Ru was found to be more active than Pt catalysts for carboxylic acids [31], phenol and aniline [32], whereas the opposite trend was observed in the ammonium CWAO [33].

In any case, considering that Ru and TiO$_2$ are cheaper than Pt and ZrO$_2$ and because of the negligible differences between catalysts, the rest of the study was carried out using the Ru/TiO$_2$ catalyst.

3.1.3. Effect of initial pH

The effect of pH over PNP oxidation was assessed at three different pH values: 2.0, 4.6 (without any pH adjustment) and 8.0. The pH was adjusted at the beginning of the reaction using either sodium hydroxide or sulphuric acid to set the initial pH at 8.0 and 2.0, respectively. The reaction was performed at 180 °C under 7.6 bar oxygen partial pressure and with an initial PNP concentration of 5 g L^{-1} over a 3 wt.% Ru/TiO$_2$ catalyst. The pH profiles for each experiment, as well as, the intermediates evolution can be found in Fig. S2 in supporting information.

It was found that the higher the initial pH, the higher the initial reaction rate: 9.0 ± 0.1 at pH = 2.0, 17.0 ± 0.1 at pH = 4.6 and 22.0 ± 0.1 mol$_{PNP}$ mol$_{Ru}$$^{-1}$ h^{-1} at pH = 8.0. Nevertheless, at the end of the experiment (480 min) neither the PNP nor the TOC conversions (94 ± 1% and 78 ± 4%, respectively) were affected by the initial pH value. These results were different from the pH effect reported by Pintar and Levec in the CWAO of substituted phenols [29], when at pH higher than the pKa, the phenolate anion was more reactive than the protonated form. Similar trends were also observed over activated carbon catalysts [16], where higher PNP conversions were achieved at basic pH. Actually, under acidic conditions, the concentration of toxic reaction intermediates was reported to be higher than under basic conditions. On the contrary, the CWAO of PNP over a Fe(III) resin [17] was favoured at pH below the pKa of PNP with 100% PNP conversion, but a lower degradation rate. The same happened upon sonophotocatalytic [34] and wet electrocatalytic oxidations [35].

Fig. 3. Evolution of the relative PNP and TOC concentrations as a function of time upon CWAO experiments under different reaction conditions (a) PNP (full symbols) and (b) TOC (empty symbols) upon CWAO at 160 °C – 7.6 bar (circles), 160 °C – 11.4 bar (triangles), 180 °C – 7.6 bar (squares) and 180 °C – 11.4 bar (diamonds). Initial PNP concentration = 5 mg L^{-1}, 0.5 g of Ru/TiO$_2$. No pH adjustment. No NaCl.

In spite of the same PNP and TOC conversions, there were several differences in the intermediate distribution. Looking at the products in the effluent when the initial pH was 2.0, a larger fraction of the reaction intermediates remained unidentified (see Fig. 5d). At pH 8.0, there was a higher fraction of non-oxidised phenolic compounds. Moreover, the biodegradable acids fraction was higher when the initial pH was 4.6. These differences could be attributed to different reaction routes, as previously reported in [16].

3.1.4. Effect of oxygen partial pressure

The effect of the oxygen partial pressure was studied at two different temperatures: 160 and 180 °C, using two different oxygen partial pressures related to the stoichiometric amount of oxygen required for complete mineralization of PNP and a 50% oxygen excess compared to the stoichiometric amount. Noteworthy, the total pressure was also kept constant all along the experiment and so re-adjusted whenever necessary, especially after each liquid sample withdrawal. All the other reaction conditions were kept constant: 3 wt.% Ru/TiO$_2$ catalyst, initial pH of 4.6 and initial PNP concentration of 5 g L^{-1}. The initial reaction rate remained almost constant for all the experiments performed at a given temperature, i.e. ca. 8 ± 1 and 18 ± 1 mol$_{PNP}$ mol$_{Ru}$$^{-1}$ h^{-1} at 160 and 180 °C, respectively. These values have been calculated from the data appearing in Fig. 3a and b. The results demonstrate that oxygen transfer from the gas to the liquid phase and from the liquid phase to the catalyst surface was not rate limiting [36].

3.1.5. Effect of ionic strength

The effect of the ionic strength of the influent on the PNP oxidation and the biodegradability enhancement was studied with two experiments carried out under the same operational conditions (180 °C, 7.6 bar P_{O_2}, initial PNP concentration of 5 g L^{-1} 3 wt.% Ru/TiO$_2$ catalyst) but using two different NaCl concentrations (0 and 25 g L^{-1}). Upon addition of sodium chloride, the initial reaction rate decreased from 18 to 13 mol$_{PNP}$ mol$_{Ru}$$^{-1}$ h^{-1}. However, at the end of the experiment (480 min), the PNP and TOC conversions and the intermediates distribution were similar in both experiments. Similarly, Béziat et al. [25] reported that inorganic salts, such as sodium chloride, slightly decreased the oxidation rate of acetic acid upon the CWAO of succinic acid. In any case, this result is very encouraging since most of the industrial effluents demonstrate high ionic strengths, as simulated here by the addition of a large amount of NaCl.

3.2. Intermediates distribution and reaction pathway

The reaction intermediates detected in this study were catechol, phenol, 4-NC, 2,4-DNP, p-BQ and fumaric, acetic, succinic, maleic and acrylic acids. Depending on the operational conditions, some of these intermediates were present in higher, lower or even null concentrations. The concentration of each intermediate and the unconverted PNP at the end of each experiment (480 min) are presented in Fig. 4. Regarding N-species, as we said before, the only intermediate detected was NO$_3$$^-$, being the TN constant, as expected. It should be mentioned that, the biological treatment proposed in this study for being after the CWAO is only based on COD removal, so that the N-species were not further studied.

Intermediates were only present in minor amounts after the WAO and CWAO experiments at 120 °C since the PNP conversion was very limited even after 480 min (Fig. 4a and b). In general, the concentration of carboxylic acids (mainly acetic and succinic) increased with increasing temperature in both WAO and CWAO experiments (Fig. 4a and b). Moreover, the use of a catalyst prevented the accumulation of 4-NC, especially at 160 °C (Fig. 4a and b). The nature of the catalysts had almost no effect on the intermediates distribution (Fig. 4c), being the only remarkable difference the accumulation of fumaric acid with the Ru-based catalysts. The increase of oxygen concentration had only a limited effect on the intermediates distribution whatever the temperature (Fig. 4d). The accumulation of 2,4-DNP increased with increasing the oxygen partial pressure, whereas maleic acid only appeared under stoichiometric oxygen partial pressure. Finally, the initial pH of the reaction mixture had a significant impact on the intermediates distribution (Fig. 4e). At basic pH (8.0), a high concentration of 4-NC accumulated in the reactor, while it was almost zero at acid pH values (2.0 and 4.6). The highest accumulation of carboxylic acids happened at pH 4.6, with mainly acetic and succinic acids. The lowest carboxylic acids accumulation happened at the lowest pH (2.0), when the highest concentration of 2,4-DNP was detected.

The identification of all by-products and intermediates formed upon reaction is critical to evaluate the toxicity and the biodegradability of CWAO effluents, as far as the residual TOC value does not provide enough information to assess these parameters. However, this is a hard task since, in the case of nitro-aromatics, the possible intermediates are quite diverse and complex and sometimes present at very low concentration, so that a proper identification and quantification becomes difficult. For that reason, the information available in the literature about the nitro-aromatics intermediates formed upon CWAO is limited [10]. It is generally
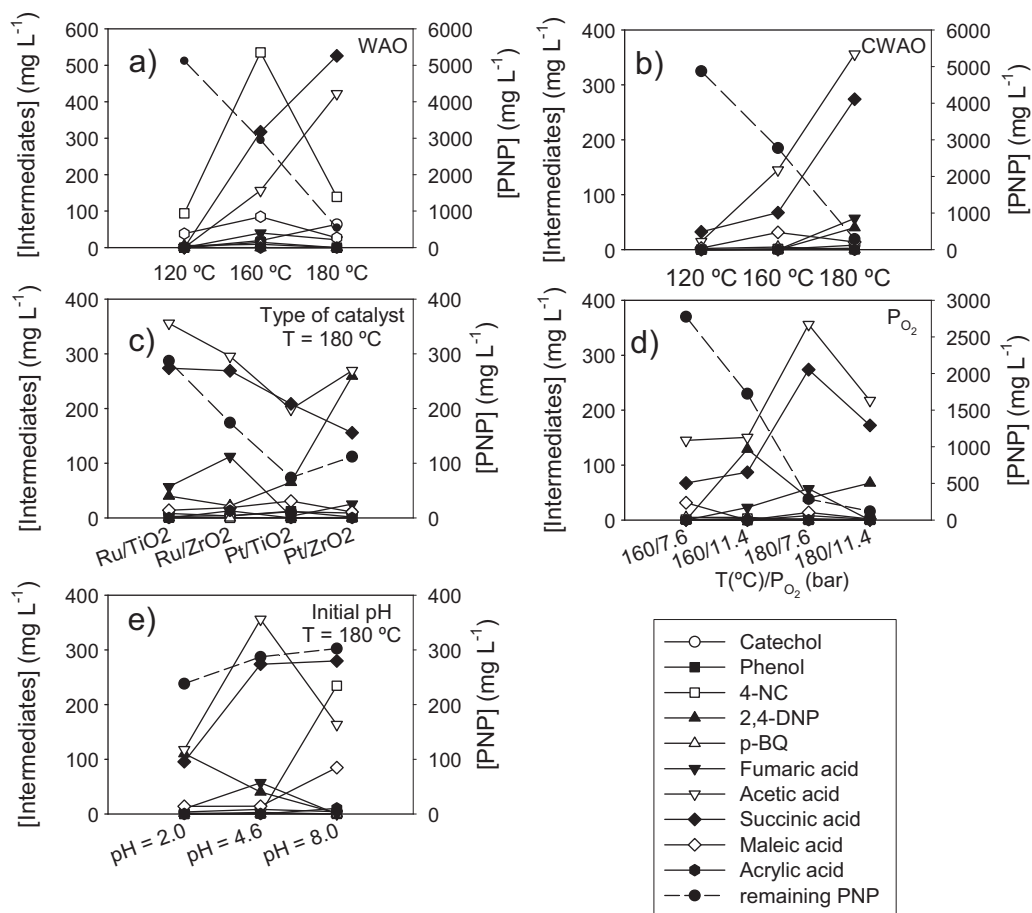
Fig. 4. Intermediates distribution at the end of the reaction (480 min) upon different experiments (see Table 1): (a) WAO experiments at different temperatures, (b) CWAO experiments at different temperatures, (c) impact of the catalyst formulation, (d) influence of oxygen partial pressure and (e) impact of the initial pH.
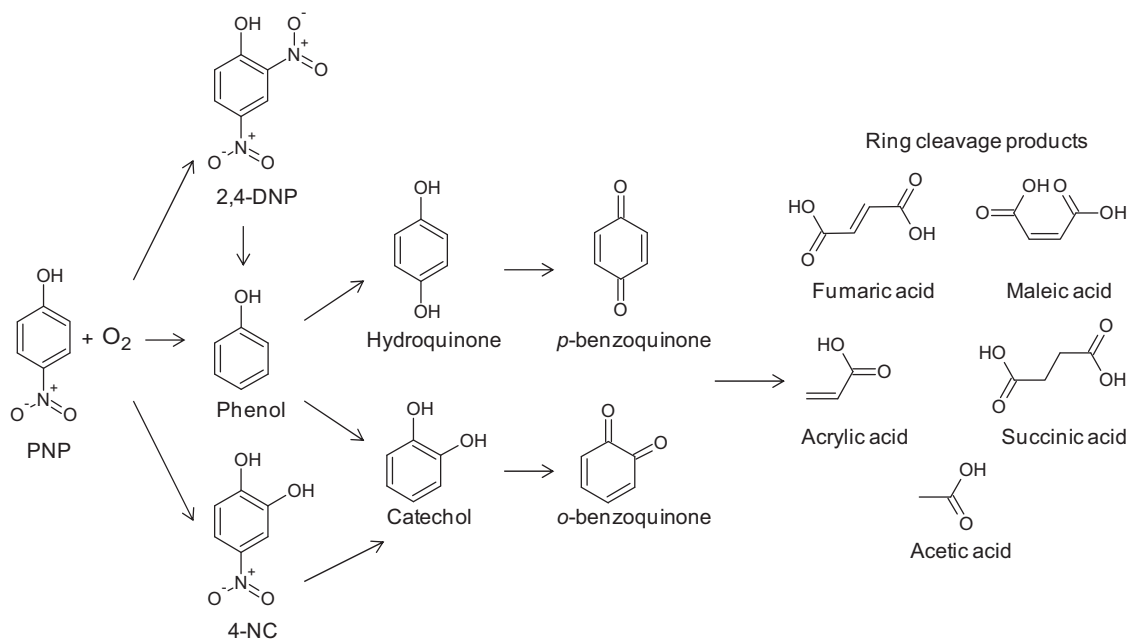
Fig. 5. Proposed reaction pathway for the CWAO of PNP.

accepted that the CWAO of phenol and aniline proceeds via a free radical mechanism [10,26,37–41]. The reaction pathway we proposed for the CWAO of PNP is schematised in Fig. 5, in line with what was established by Pintar and Levec [29] in the CWAO of substituted phenols and aniline. In that study, PNP was indeed found to be an intermediate in the aniline CWAO and the results observed in our study confirmed that the reaction pathway might follow the same free radical mechanism, as the one observed in the CWAO of phenol and aniline.

In the proposed pathway, the first step would be the cleavage of the N—C bond to give a phenoxy radical. Then, the formation of 2,4-DNP and 4-NC could be explained by the presence of the nitro group, which has an electron withdrawing effect in the *para* position of the aromatic ring, reducing partially the effect of the hydroxyl group, and therefore, reducing the rate of the electrophilic attack and the subsequent formation of catechol and hydroquinone. This effect was also reported by Collado et al. [38] but using *p*-hydroxybenzoic acid, which also presents the same electron withdrawing effect. Thus, by a resonance effect of the PNP molecule, the nitro group would be a *meta* directing group since the substitution on the *ortho* and *para* positions would be less stable. This could be the reason why, under the tested conditions, the formation of phenoxy radicals was hindered by steric effect of the nitro group. As a result, 4-NC was formed by the electrophilic attack of the PNP molecule at the early stages of the oxidation. Later on, the rupture of the N—C bond in 4-NC led to the formation of catechol, as shown in Fig. 5. After catechol and hydroquinone were formed, a subsequent proton transfer led to *p*-BQ and the unstable *o*-benzoquinone. Later the C—C bond breaking led to ring opening products, mainly carboxylic acids. As we said in Section 3.1.1, the presence of NO_3^-, can be explained by the oxidation of NO_2^-, which comes from the PNP, 4-NC and 2,4-DNP molecules. As expected the total nitrogen remained constant.

Other oxidation processes, like electrochemical, electrocatalytic and microwave assisted oxidations also followed a free radical mechanism through phenoxy radicals as well, but with different termination steps and resulting in different intermediates [36,42–45].

3.3. PNP CWAO effluents and intermediates biodegradability

In a previous study, a new methodology based on respirometry was established to classify the reaction intermediates formed upon CWAO into readily biodegradable, inert and toxic/inhibitory compounds, according to their effect on the specific oxygen uptake rate (SOUR) and the oxygen consumption (OC) [13]. In this former study, the reaction intermediates presenting a similar OC (for the same initial COD concentration) to a readily biodegradable control substrate (acetic acid) were considered as readily biodegradable intermediates. When the compounds were not readily biodegradable, but did not have any toxic or inhibitory effect over the consumption of the control substrate, they were classified as inert intermediates at the tested concentrations. These inert intermediates could be slowly biodegraded but to confirm it, a different and high-time consuming experiment would have been necessary. Finally, when the intermediates showed a negative effect over the consumption of the control substrate, they were classified as toxic or inhibitory for a further biological treatment. Following the same methodology, some of the reaction intermediates identified in the present study could be separated according to this classification.

However, PNP and other intermediates such as: 4-NC, acrylic acid and 2,4-DNP had not previously been tested and subsequently classified. Therefore, using the respirometric procedure previously described (Section 2.4), PNP was classified as an inert compound since its COD_{RB} was just $2.2 \pm 0.7\%$, exhibiting a slight inhibitory effect and only a moderate toxic effect at $47 \, mg \, COD \, L^{-1}$.

For 4NC and 2,4-DNP, the toxic and inhibitory effects were less than 5% at $47 \, mg \, COD \, L^{-1}$. Consequently, both compounds were classified as inert intermediates. Finally, acrylic acid effect was studied at different concentrations between 26 and $107 \, mg \, COD \, L^{-1}$. The $\%COD_{RB}$ was around 20%, which could allow its classification as a biodegradable intermediate. However, at high concentration, acrylic acid also exhibited a marked inhibiting effect (up to 80% at $107 \, mg \, COD \, L^{-1}$) and consequently, it was classified as an inhibitory intermediate.

According to our previous results [14] and the respirometric tests carried out in this study, the intermediates of the PNP oxidation were classified as: (i) readily biodegradable compounds: acetic, fumaric, and succinic acids; (ii) inert compounds: PNP, phenol, catechol, 4-NC, 2,4-DNP and maleic acid; (iii) toxic/inhibitory compounds: p-BQ and acrylic acid. For obvious reasons, the individual effect of the unidentified compounds could not be determined.

In order to establish the optimal conditions for a combined chemical–biological treatment, respirometric tests were performed on all the CWAO effluents described in Section 3.1. The objective was to find the best operational conditions in terms of biodegradability enhancement that would allow a successful coupling with a subsequent biological treatment. The readily biodegradable COD fraction (COD_{RB}) was calculated using the procedure detailed in Section 2.4.

Figure 6 shows the $\%COD_{RB}$ of each effluent together with the corresponding intermediate distribution, according to the classification obtained from the respirometric tests. Both effluents obtained upon WAO (Fig. 6a) and CWAO (Fig. 6b) at 120 °C exhibited a negligible $\%COD_{RB}$. The effect of increasing the temperature was remarkably higher on the $\%COD_{RB}$, i.e. in terms of biodegradability, than on the TOC and PNP conversions. For instance, the $\%COD_{RB}$ upon CWAO with a Ru/TiO$_2$ catalyst (Fig. 6b) increased from 4% at 120 °C to 30% at 160 °C and 61% at 180 °C. These results are in agreement with what was found in the CWAO of phenol and o-cresol by Suárez-Ojeda et al. [14], when it was demonstrated that an increase in temperature and the use of a catalyst improved the biodegradability, because of the higher concentration of readily biodegradable intermediates. However, the $\%COD_{RB}$ achieved in this study using noble metal catalysts was higher than the one reported by Suarez-Ojeda et al. using activated carbon (AC) as catalyst [14]. Consequently, the use of noble metal catalysts improved the biodegradability of the CWAO effluents compared to other catalysts such as AC. The results obtained upon WAO and CWAO at 160 and 180 °C were clearly different in terms of biodegradability, despite the small increase of temperature (Fig. 6a and b). The reason is the extraordinary increase of the biodegradable intermediates fraction obtained with the increase of temperature. Moreover, the $\%COD_{RB}$ values (55–60%) achieved after WAO or CWAO at 180 °C were very similar or even better than those obtained for an urban wastewaters. Consequently, these effluents could clearly be considered as biodegradable.

The use of different catalysts had only a slight influence on the biodegradability enhancement since the $\%COD_{RB}$ obtained with the four different catalysts was very similar: 61% for Ru/TiO$_2$, 56% for Ru/ZrO$_2$, 64% for Pt/TiO$_2$ and 60% for Pt/ZrO$_2$. However, there seems to be a slight relationship between the support and the biodegradability enhancement, being the catalysts supported on TiO$_2$ the one leading to the effluents with the highest biodegradability.

The effect of P_{O_2} was also almost negligible since the $\%COD_{RB}$ values were almost the same (Fig. 6c). Nevertheless, there was an important increase of the unidentified intermediates fraction with the increase of P_{O_2}.

The effect of pH on the biodegradability enhancement is shown in Fig. 6d. The highest fraction of biodegradable intermediates and, consequently, the highest $\%COD_{RB}$ was obtained at an initial pH of 4.6, which was the natural pH of the PNP solution without any
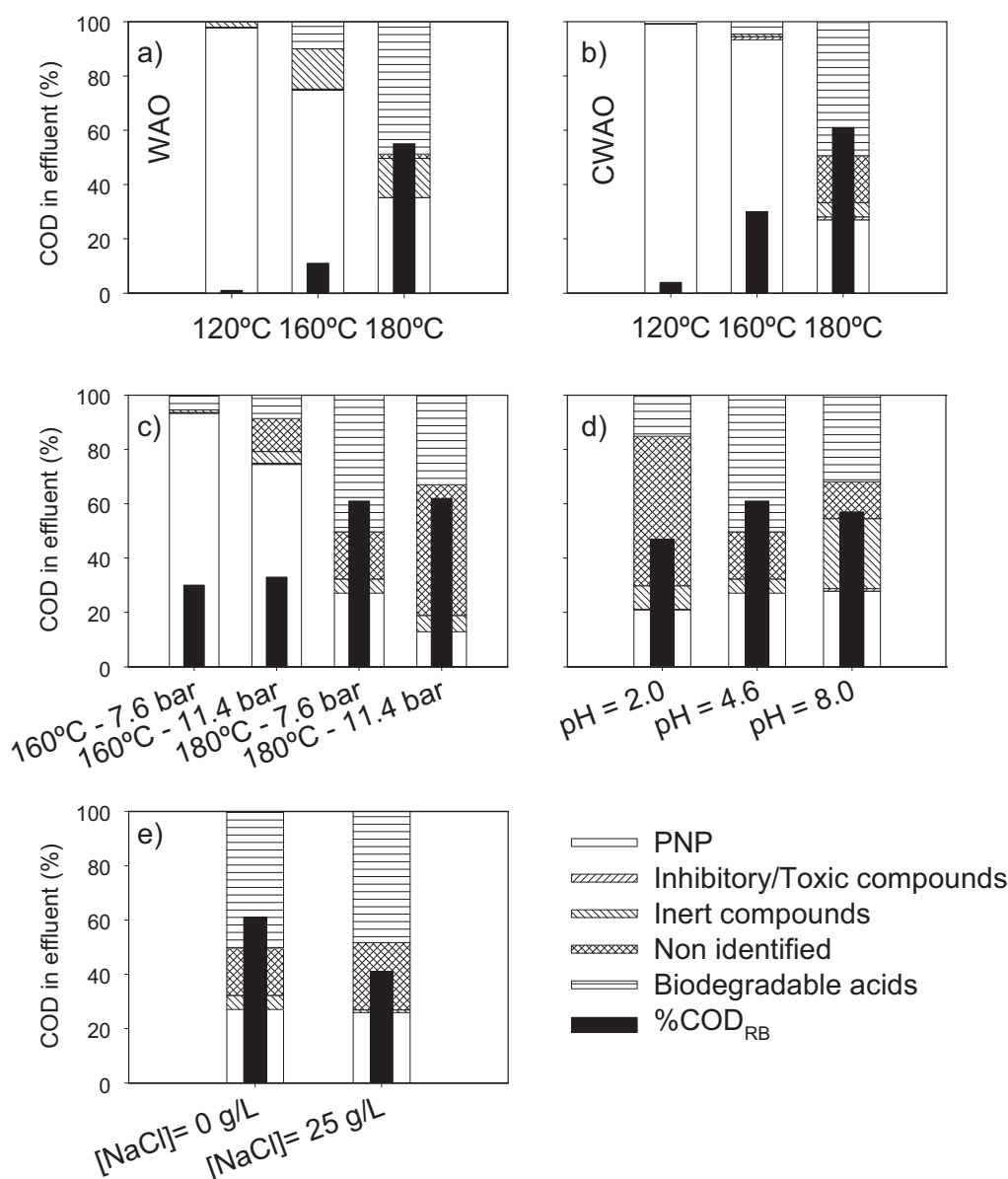
Fig. 6. Intermediates distribution in terms of biodegradability and %CODRB in the WAO and CWAO effluents: (a) WAO experiments at 120 °C – 7.6 bar of oxygen partial pressure; 160 °C – 7.6 bar of oxygen partial pressure; 180 °C – 7.6 bar of oxygen partial pressure; (b) CWAO over Ru/TiO$_2$ at 120 °C – 7.6 bar of oxygen partial pressure; 160 °C – 7.6 bar of oxygen partial pressure; 180 °C – 7.6 bar of oxygen partial pressure; (c) CWAO experiments at 160 and 180 °C under stoichiometric or excess oxygen; (d) CWAO experiments at 180 °C, 7.6 bar of oxygen partial pressure at different initial pH values and (e) CWAO experiments at different NaCl concentrations. Initial PNP concentration: 5 g L^{-1}, 0.5 g of Ru/TiO$_2$.

pH adjustment. Nevertheless, the %COD$_{RB}$ achieved at pH 2.0 and 8.0 were also high (40–50%), which means that these effluents were also clearly biodegradable. The most remarkable difference was the high fraction of unidentified intermediates obtained at an initial pH value of 2.0.

Finally, the presence of NaCl in high concentration in the reaction medium did not affect the performances of the CWAO process in terms of PNP and TOC conversions. However, the biodegradability decreased and the %COD$_{RB}$ was reduced by 20% (Fig. 6e). In this case, the difference could not be attributed to any change in the intermediates fraction, which were very similar (Fig. 6e), but to a negative effect of NaCl over the biomass in the respirometric test [47].

In spite of the different results, all CWAO effluents obtained at 180 °C demonstrated a %COD$_{RB}$ higher than 40%. This was a major result since the success of the biological treatment of industrial

effluents with %COD$_{RB}$ lower 25% has already been reported [13,46]. When selecting the most appropriate CWAO conditions for providing the most suitable effluent for a further biological treatment, it must be considered not only the PNP removal or TOC conversions, but also the intermediates distribution and, consequently the %COD$_{RB}$. However, after evaluating all the operating parameters, if all of them meet the biodegradability requirements, the optimum conditions would be the one with the lowest running costs. From this study, it can be concluded, that the most suitable conditions would be to operate the oxidation at 180 °C under a stoichiometric P_{O_2}. About the catalyst, there was no significant difference between the four catalysts, but Ru/TiO$_2$ seemed to be the best in terms of cost. Regarding the pH, there is no need of any pH adjustment before the CWAO since no improvement was observed under acid or basic conditions. Finally, the impact of the saline content should be further studied to properly establish the impact

on the CWAO process, and also over the biomass in the biological WWTP.

4. Conclusions

Several conditions were investigated for the WAO and CWAO of PNP. Conversion was higher than 90% for most of the tested conditions. Temperature was found to be the most important operating parameter upon CWAO, being the activation energy ca. 57 ± 1 kJ mol^{-1}. The PNP oxidation was not much influenced by the oxygen partial pressure. All the catalysts exhibited a similar behaviour in terms of PNP and TOC conversions; however, the initial reaction rate was slightly higher over the platinum-based catalysts. The identification of the oxidation intermediates allowed establishing a reaction pathway proceeding through a free radical mechanism.

In relation to the biodegradability enhancement of the high-strength PNP wastewater, CWAO increased the biodegradability by more than 50% in most of the conditions tested. The carboxylic acid fraction was determined as a key factor to be taken into account, as the best biodegradability enhancement was observed when this fraction was the highest. The partial pressure of oxygen also had a negligible effect on the biodegradability enhancement. Even though the ionic strength did not affect the CWAO performance, the presence of NaCl decreased the effluent biodegradability. In terms of pH, the most suitable scenario was the one with no pH adjustment.

An integrated CWAO and biological treatment would certainly allow an easy removal of reaction intermediates formed during the first step of the treatment. The best CWAO conditions for such a pre-treatment of the high-strength PNP wastewater would be to work at 180 °C under a stoichiometric oxygen partial pressure (7.6 bar P_{O_2}) using a Ru/TiO$_2$ catalyst.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2012.04.001.

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